



Study of extraction and purification of Ni, Co and Mn from spent battery material

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ABSTRACT

In spent battery material, there are plenty of valuable metals, such as copper, nickel, cobalt, manganese. Recovery of valuable metals from spent battery material not only protects the environment but also improves the utilization of resources and decreases the cost of battery material. In this study, hydrochloric acid is used as lixiviant with characteristics of faster leaching rate and being recycled easily. The optimal conditions are that hydrochloric acid concentration is 6 mol/L, reaction temperature is exactly 60 °C, liquid/solid ratio is 8:1, (H₂O₂)_{mol}/(MeS)_{mol} = 2, and the leaching time is 2 h, the results show that the dissolution yields of Ni, Co and Mn can be 95 wt.% at least. The basic purification concept of the leaching solution includes that copper is removed through replacement by iron powder followed by iron precipitation in goethite method. The results show that Cu and Fe can be removed 99 wt.% at the least. At the same time, the loss of Ni, Co and Mn is not beyond 2 wt.%, 3 wt. and 2 wt.%, respectively. This method makes the preparation of pure Ni_xCo_yMn_z ternary system precursor economical. The process seems to be able to claim base metals from waste in a reliable and feasible way.

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1. Introduction

Nickel and Cobalt are very important metals applied in many fields, such as energy material and functional material. The world demand for metals is progressively increasing, while primary resources are being depleted. With the constraints raised by Law and related legislation assigned to protect the environment from hazardous wastes in the world, it becomes more and more important to partly satisfy such world demand through recovery of metals of concern from secondary resources such as spent magnetic material, waste alloy (Tan and Shen, 2000), waste nickel scraps (Yunjian et al., 2006) and spent battery material (Rabah et al., 2008). Compared with raw ore, waste material has high content of nickel, cobalt, manganese and etc. and its composition is very complicated due to different wastes. Many methods are applied for dealing with these wastes, such as leaching with sulphuric acid (Pietrelli and Bellomo, 1999; Yunjiao et al., 2008), mixed acid (Yanting et al., 2005), electrolysis method (Lupi and Pasquali, 2003) etc. There are many purification methods for the separation of impurities from leaching solution, such as solvent extraction (Douglas, 2005; Preston and du Preez, 2000), ion exchange (Mendes and Martins, 2005; Seggiani et al., 2006), precipitation with sulfide (Henry et al., 2003) or alkali (Giannopoulou and Panias, 2008).

Ni_xCo_yMn_z cathode material for lithium ion battery is an excellent material and is applied more and more extensively in lithium ion battery industry. Traditionally, Ni_xCo_yMn_z cathode material is prepared by pure

chemical reagent which is relatively expensive. With shortage of raw resources and increase of chemical reagent price, it is more and more important to recycle valuable metals from waste or recover metals from raw ores for preparation of battery materials. Liu Yun-jian (Yunjian et al., 2006) even prepared satisfied LiCoO₂ from waste battery material and Qin Wen-qing (Wenqing et al., 2005) prepared lead sulfate powders from galena concentrates directly. The aim of this work is to recover nickel, cobalt and manganese metals and/or some of their valuable salts from spent battery material which come from some plants in China. A hydrometallurgical technique was used in this experiment. Hydrochloric acid was used as lixiviant in this process. A particular advantage of the leaching process is that hydrochloric acid as a lixiviant allows comparatively easier recovery of the useful free acid from its waste solution than sulphuric acid does. Moreover, separation of metal chlorides through solvent extraction is much easier than from sulphate medium (Olanipekun, 2000). In this paper, the effect on leaching yields on hydrochloric acid concentration, liquid/solid ratio, temperature, acidity and oxidant concentration are discussed. Besides, the purification conditions of removal of copper and iron are also introduced in this paper. The leaching solution after purification can be used to prepare the precursor of Ni_xCo_yMn_z cathode material directly which can decrease the cost of Ni_xCo_yMn_z cathode material obviously.

2. Experimental

2.1. Materials

The composition of spent battery material obtained from a battery material plant is shown in Table 1. Fig. 1 shows that the waste contains cobalt oxide, nickel oxide, manganese sulfide, ferric and ferrous oxide,

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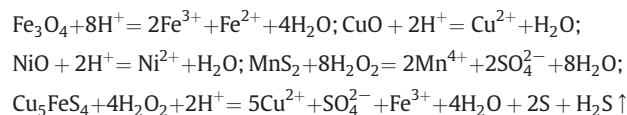
Table 1
Chemical composition of spent battery material.

Composition	Ni	Fe	Cu	Co	Mn	Ca	Mg	Acid insoluble
wt.%	20	10	20	20	5	0.26	0.37	24.37

copper oxide and copper iron sulfide as depicted from the X-ray pattern. Acid insoluble components are mainly some silica and refractory materials which were applied in material sintering. The waste samples were crushed and screened into 120 μm through mesh.

2.2. Experimental principle

In leaching process, some reactions can occur as follows:



2.3. Experimental method and experimental procedure

Chemical grade hydrochloric acid and hydrogen peroxide (30 vol.%) as oxidant were used in this study. The amount of H_2O_2 added

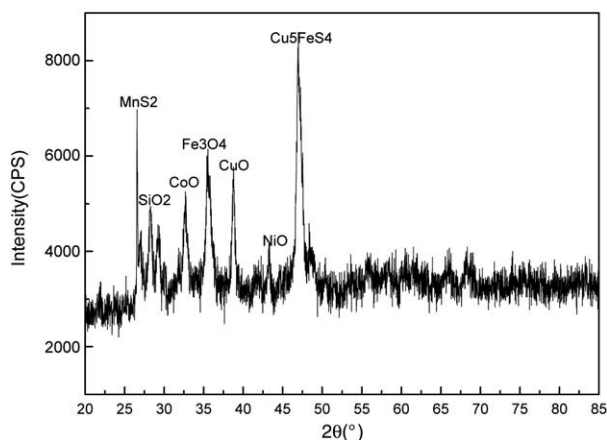


Fig. 1. XRD pattern of spent battery material.

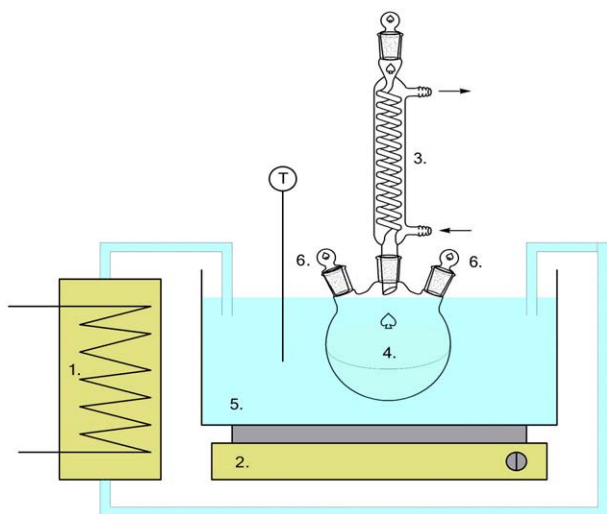


Fig. 2. Equipment sketch: 1. temperature-controlled bath with external flow; 2. magnetic stirrer; 3. tap water-cooled condenser; 4. round-bottom flask with 3 holes; 5. water bath; 6. outlets for batch addition and solution sampling.

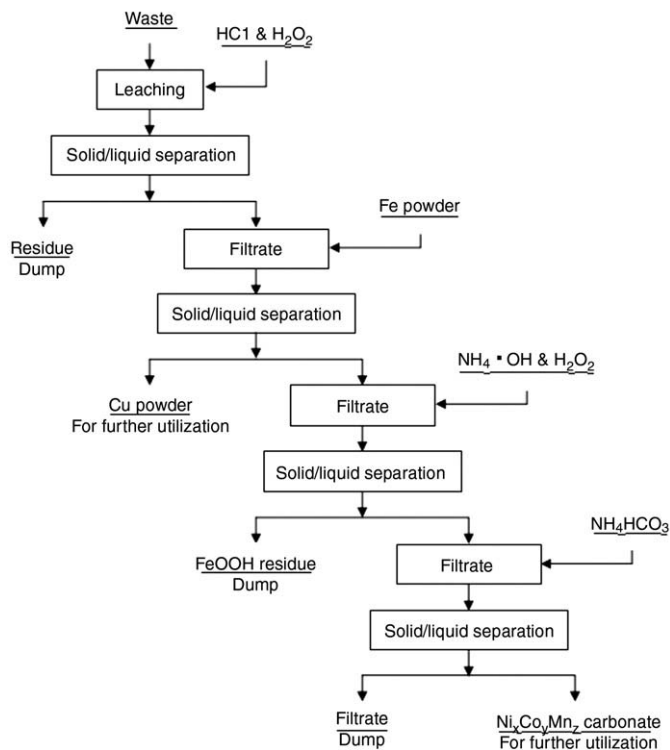


Fig. 3. Flowsheet for Ni, Co and Manganese recovery.

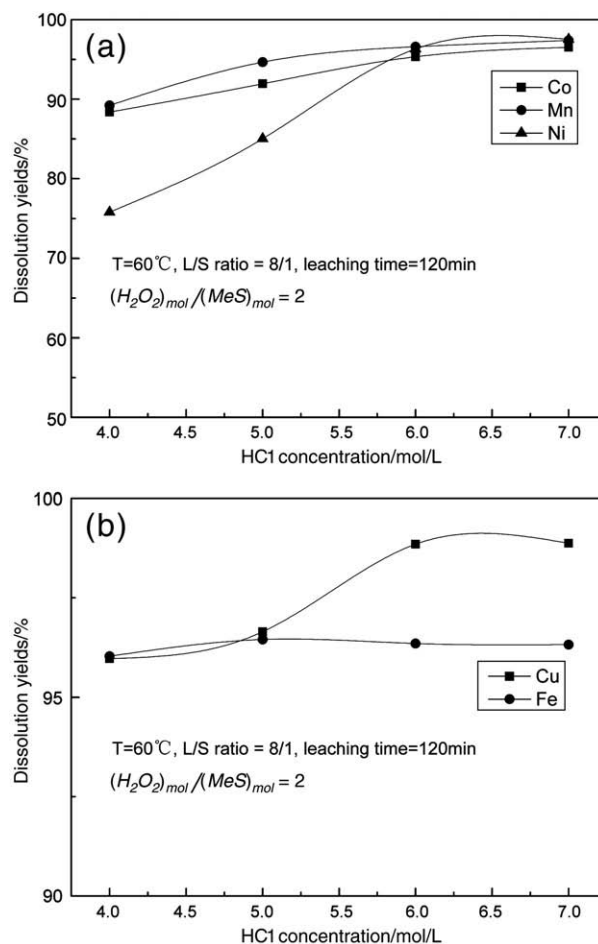


Fig. 4. (a) Effect of HCl concentration on Ni, Co and Mn dissolution yields. (b) Effect of HCl concentration on Cu and Fe dissolution yields.

through outlets by dropping was calculated with the mole number with contrast of the content of MeS in waste. The reaction between spent battery material and hydrochloric acid was performed in a 1000-mL round-bottom flask with 3 holes. The reaction temperature was maintained constant in water heated by electric heater with a thermostatically controlled water bath, equipped with a digitally controlled thermometer (within ± 0.5 °C). The reaction mixture was agitated at a rate of 250 rpm. The equipment sketch was shown in Fig. 2. And the experimental procedure was shown in Fig. 3.

2.4. Analysis

Analysis of the spent batteries, metal ions: Co, Ni and Mn in solution and end products were carried out by chemical titration, Cu and Fe were determined by titration and with the help of atomic absorption techniques type of Ruili-wfx120. A computerized X-ray diffraction equipment (XRD, Rint-2000, Rigaku) was used to identify the spent battery components and leaching residue components.

3. Results and discussion

3.1. Leaching conditions

3.1.1. Effect of HCl concentration on dissolution yields

It can be seen in Fig. 4 that the leaching yields increase gradually with increase of HCl concentration except Fe. The maximum

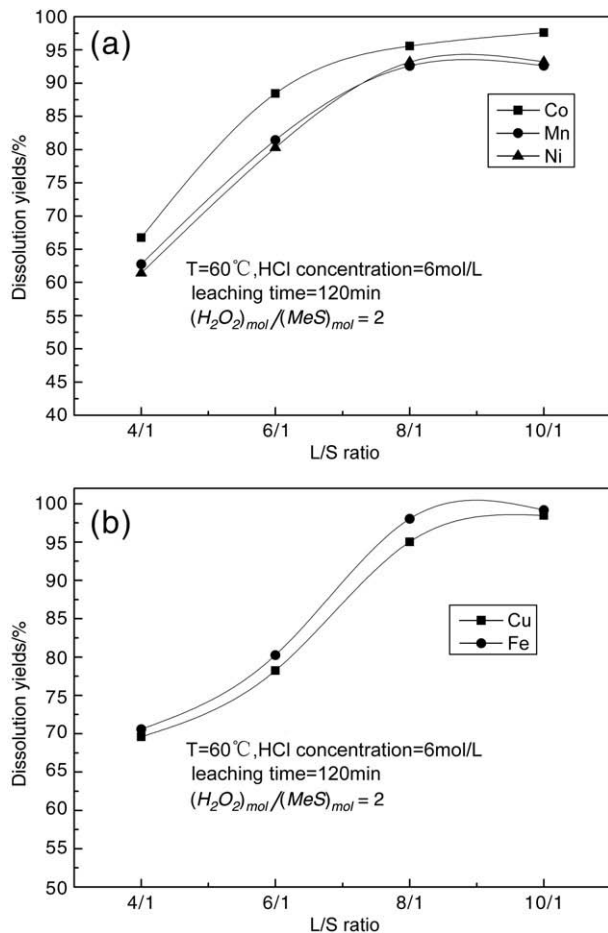


Fig. 5. (a) Effect of L/S ratio on Ni, Co and Mn dissolution yields. (b) Effect of L/S ratio on Cu and Fe dissolution yields.

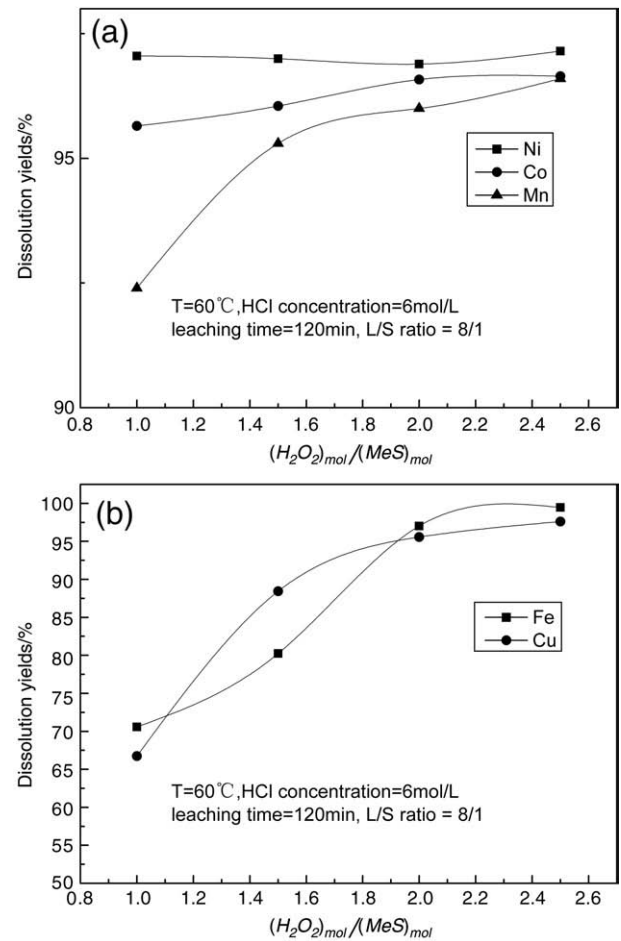


Fig. 6. (a) Effect of $(H_2O_2)_{mol}/(MeS)_{mol}$ on Ni, Co and Mn dissolution yields. (b) Effect of $(H_2O_2)_{mol}/(MeS)_{mol}$ on Cu and Fe dissolution yields.

dissolution yields can reach 96.5 wt.% with nickel, 95.5 wt.% with cobalt, 98.5 wt.% with copper, 96 wt.% with manganese and about 96.3 wt.% with iron. It is worthy noting that the maximum leaching yields are not affected when the acid concentration is beyond 6 mol/L. The optimum concentration of HCl is 6 mol/L.

3.1.2. Effect of L/S ratio on dissolution yields

Fig. 5 shows that the leaching yields increase with increasing of L/S ratio obviously, but not changes when L/S ratio is beyond 8:1. Because increasing of L/S ratio can decrease the concentration of metal ion in leaching solution, this can strengthen mass transfer which accelerate the leaching rate. But when L/S ratio is too high is not favorable to subsequent operation. The suitable L/S ratio is 8:1.

3.1.3. Effect of H_2O_2 content on dissolution yields

Fig. 6 shows that the content of oxidant H_2O_2 has different influence on different metals in the waste while other conditions are fixed. With increase of H_2O_2 content, the leaching yields of all metals increase obviously except nickel and cobalt. In this leaching process, sulfide ion can be released and react with metal ions which are insoluble and hydrogen ions which emit in gas, which is shown in chemical reaction formulas 1 and 2. To improve leaching yields of waste, one way is to increase acid amount which is proved in Figs. 4 and 5, the other way is to add oxidant which can react with sulfide and generate sulfate. With increase of oxidant content, the leaching yields of Fe, Mn and Cu increase much more than that of Ni and Co, this can be explained well while Fe, Mn and Cu exist in MeS form in waste which are shown in Fig. 1. When

$(\text{H}_2\text{O}_2)_{\text{mol}}/(\text{MeS})_{\text{mol}} \geq 2$, the maximum of dissolution yields can be attained.



3.1.4. Effect of temperature on dissolution yields

The effect of temperature on dissolution yields can be seen in Fig. 7 and the other conditions are fixed. It can be seen in Fig. 7 (a) that the leaching yields of Ni and Co are not affected greatly by reaction temperature, the leaching yields of Ni and Co can reach 95 wt.% when temperature is beyond 60 °C. But the leaching of Fe, Cu and Mn are affected greatly by oxidant content, and H_2O_2 oxidant is decomposed easily when temperature increases. Although the leaching rate can be improved with increase of temperature, the dissolution yields of Fe, Cu and Mn descend below 90 wt.% when temperature is 90 °C due that H_2O_2 oxidant is decomposed greatly. The optimum temperature is 60 °C.

3.1.5. Effect of leaching time on dissolution yields

At other conditions fixed, the effect of leaching time on dissolution yields can be seen in Fig. 8. Fig. 8 (a) shows that the dissolution yields of Ni and Co can achieve a satisfied result in 40 min and Ni extraction can reach the highest value after 60 min. The result can be explained

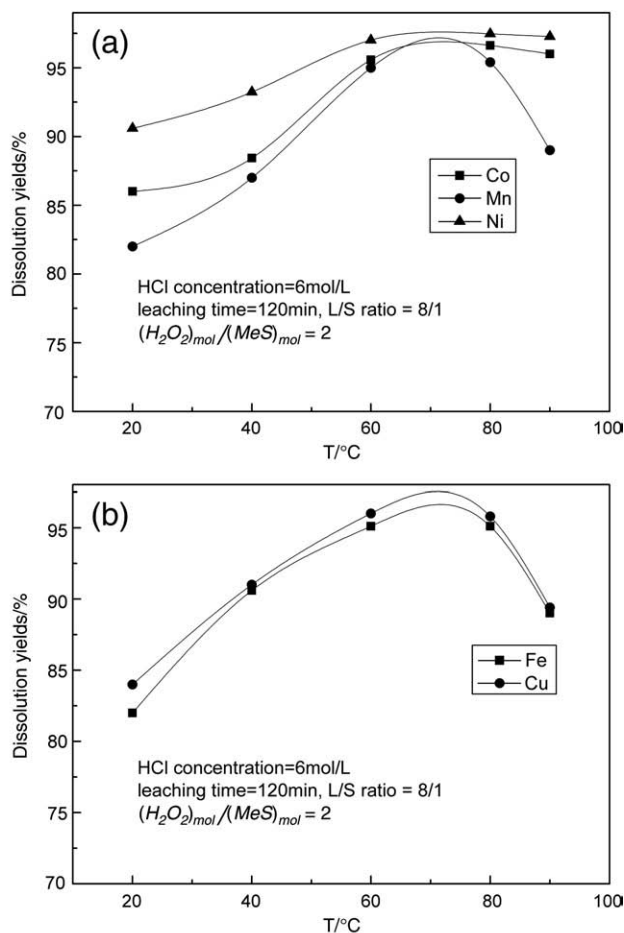


Fig. 7. (a) Effect of temperature on Ni, Co and Mn dissolution yields. (b) Effect of temperature on Fe and Cu dissolution yields.

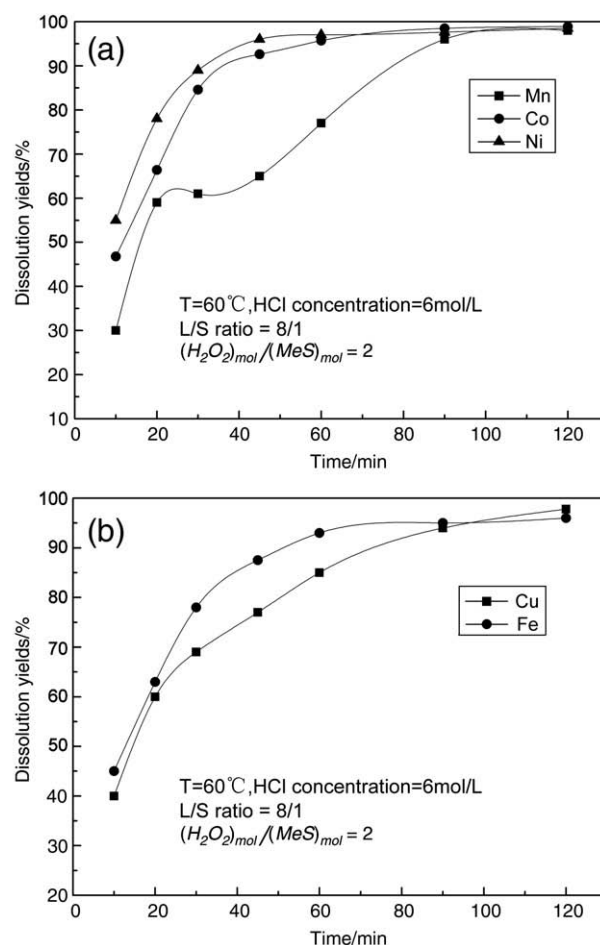


Fig. 8. (a) Effect of leaching time on Ni, Co and Mn dissolution yields. (b) Effect of leaching time on Fe and Cu dissolution yields.

that initial acid concentration is relatively high and Ni and Co which mainly exist in oxide form shown in Fig. 9 can react with HCl acid without help of H_2O_2 , this makes the leaching yields and leaching rate of Ni and Co reach to the maximum value in relatively short leaching time. As shown in Fig. 9, iron and copper in waste are in form of oxide and sulfide, and metal oxide reacts with HCl acid at initial period. Fig. 8 (b) shows that the copper iron sulfide begins to react with H_2O_2 oxidant in acid solution with reaction proceeding, so the leaching yields of Fe and Cu are always increasing in the whole reaction process. MnS_2 reacts with H_2O_2 in acid solution and generates Mn_2O_3 solid shown in Fig. 8, and Mn_2O_3 thereupon is dissolved in acid solution. So the leaching yields of Mn presents a mediate plateau in the whole leaching curve in Fig. 8 (a). Fig. 9 indicates that there are some different complicate chemical phases with oxide and sulfide in material and leaching residue come from different leaching time.

3.2. Removal of copper and iron

The leaching solution contains large quantities of valuable metals, such as Ni, Co and Mn, as well as impurities, Cu and Fe. The copper is removed through replacement by iron powder and the iron is removed by precipitation in goethite form.

3.2.1. Removal of copper by iron powder replacement

The experiments show that the optimum conditions of Cu removal is that the temperature is 30 °C, the amount of Fe powder is 1.5 M times vs. the amount of copper, reaction time is 30 min, the concentration of copper in the de-copper solution can reach 0.175–0.746 ppm which accords with the demand of purification. And the

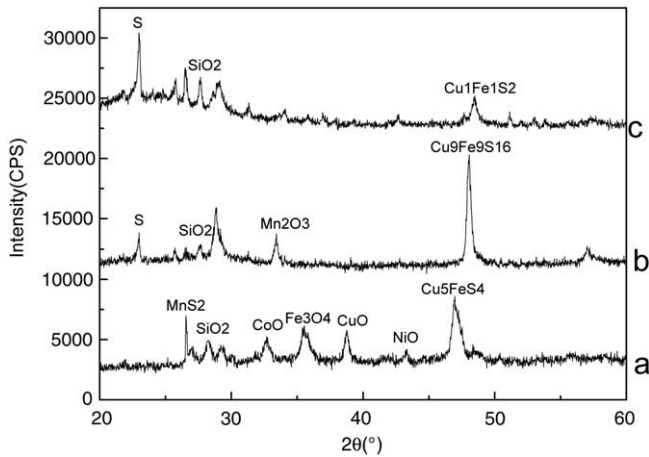
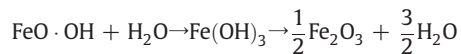
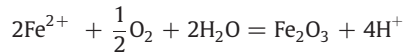
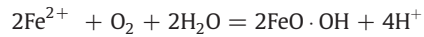


Fig. 9. XRD pattern of material and leaching residue (a material; b leaching residue after 1 h; c leaching residue after 2 h).

loss of nickel and cobalt is not beyond 0.6 wt.% and 0.4 wt.%, respectively. The XRD pattern of copper residue is shown in Fig. 10 where nickel and cobalt are nearly not detected.

3.2.2. Removal of iron by precipitation in goethite form

The removal of iron is a very important content in conventional purification process in nonferrous metal metallurgy field. There are three traditional precipitation methods which include jarosite (Dutrizac, 1996), goethite (Ismael and Carvalho, 2003) and hematite (Dutrizac and Riveros, 1999), and each method has its own application field and characteristics. In this study, the precipitation reaction is accomplished at high temperature through pH increasing with addition of oxidation reagent which is helpful to form goethite and hematite precipitates, as follows:



The optimum conditions are that precipitation terminal pH is 4, reaction temperature is 90 °C, and reaction time is 6 h. The 99 wt.% of iron can be removed, and at the same time the loss of nickel, cobalt and manganese are not beyond 2 wt.%, 3 wt.% and 2 wt.%, respectively. The precipitate formed in the process is easily filterable and mainly

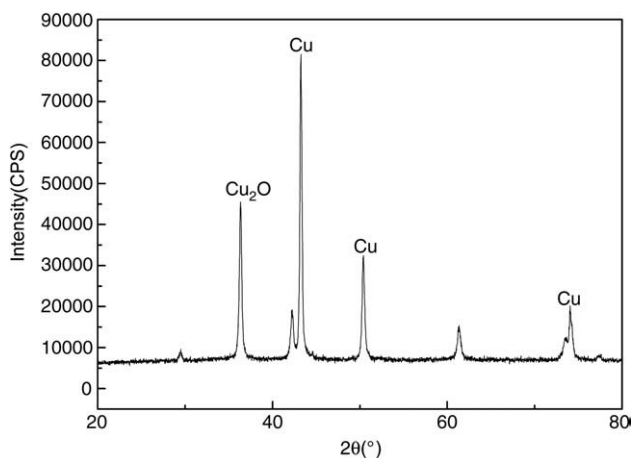


Fig. 10. XRD pattern of Cu residue.

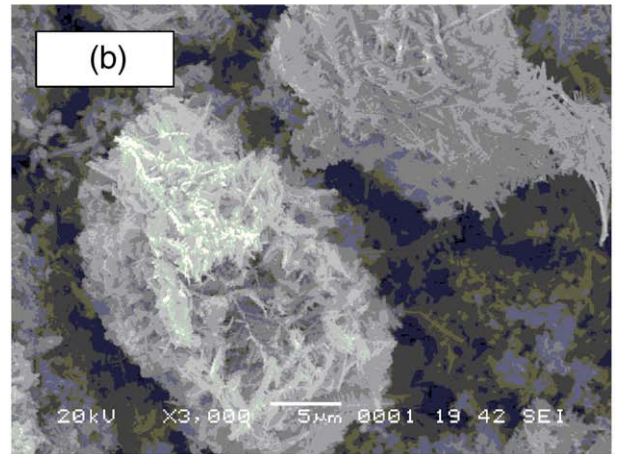
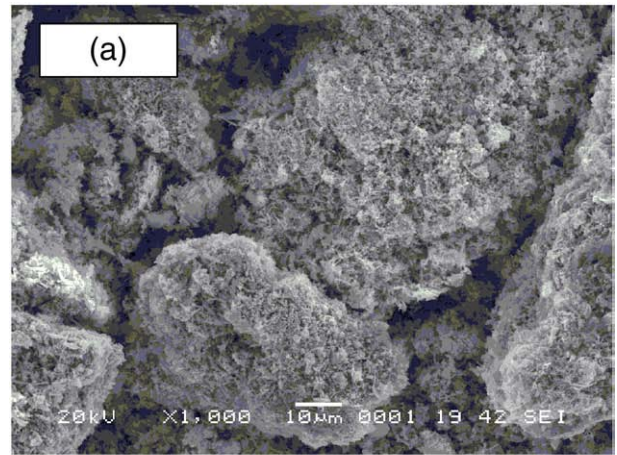


Fig. 11. The SEM graph of precipitate.

goethite precipitate and trace of hematite precipitate which can be seen in Fig. 11.

3.3. Preparation of battery material

After purification, the leaching solution mainly contains Ni, Co and Mn, the concentration of Fe and Cu has decreased to 8.32×10^{-3} g/L and 6.48×10^{-3} g/L, respectively, which follows the demand of preparation of battery material. According to the requirement of different $\text{Ni}_x\text{Co}_y\text{Mn}_z$ ratio, some amount of nickel chloride, manganese chloride and cobalt chloride are put into the solution. And it can be used to prepare the precursor of $\text{Ni}_x\text{Co}_y\text{Mn}_z$ cathode material directly through co-precipitation with addition of ammonium bicarbonate. It is qualified by the demand of $\text{Ni}_x\text{Co}_y\text{Mn}_z$ cathode material precursor prepared with pure chemical.

4. Conclusion

- (1) The optimum leaching conditions for the spent battery material are: $T = 60$ °C, $(\text{H}_2\text{O}_2)_{\text{mol}}/(\text{MeS})_{\text{mol}} = 2$, hydrochloric acid concentration = 6 mol/L, L/S ratio = 8/1, leaching time = 120 min. At this conditions, the dissolution yields of Ni, Co and Mn can be 95 wt.% at least.
- (2) The optimum Cu removal conditions are: $T = 30$ °C, $\text{Fe}_{\text{mol}}/\text{Cu}_{\text{mol}} = 1.5$, reaction time = 30 min. The optimum Fe removal conditions are: precipitation terminal pH = 4, $T = 90$ °C, reaction time = 6 h. The results show that Cu and Fe can be removed 99 wt.% at least. At the same time, the total loss of Ni, Co and Mn are not beyond 2 wt.%, 3 wt. and 2 wt.%, respectively.

- (3) This study establishes the optimum recovery of valuable metals conditions with spent battery material as resources and supplies a reference for other spent material utilization. The leaching solution can be used to prepare the precursor of $\text{Ni}_x\text{Co}_y\text{Mn}_z$ cathode material directly after purification and separation of impurities, the cost is competitive with the market price for the same chemicals prepared from primary resources.

Acknowledgements

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